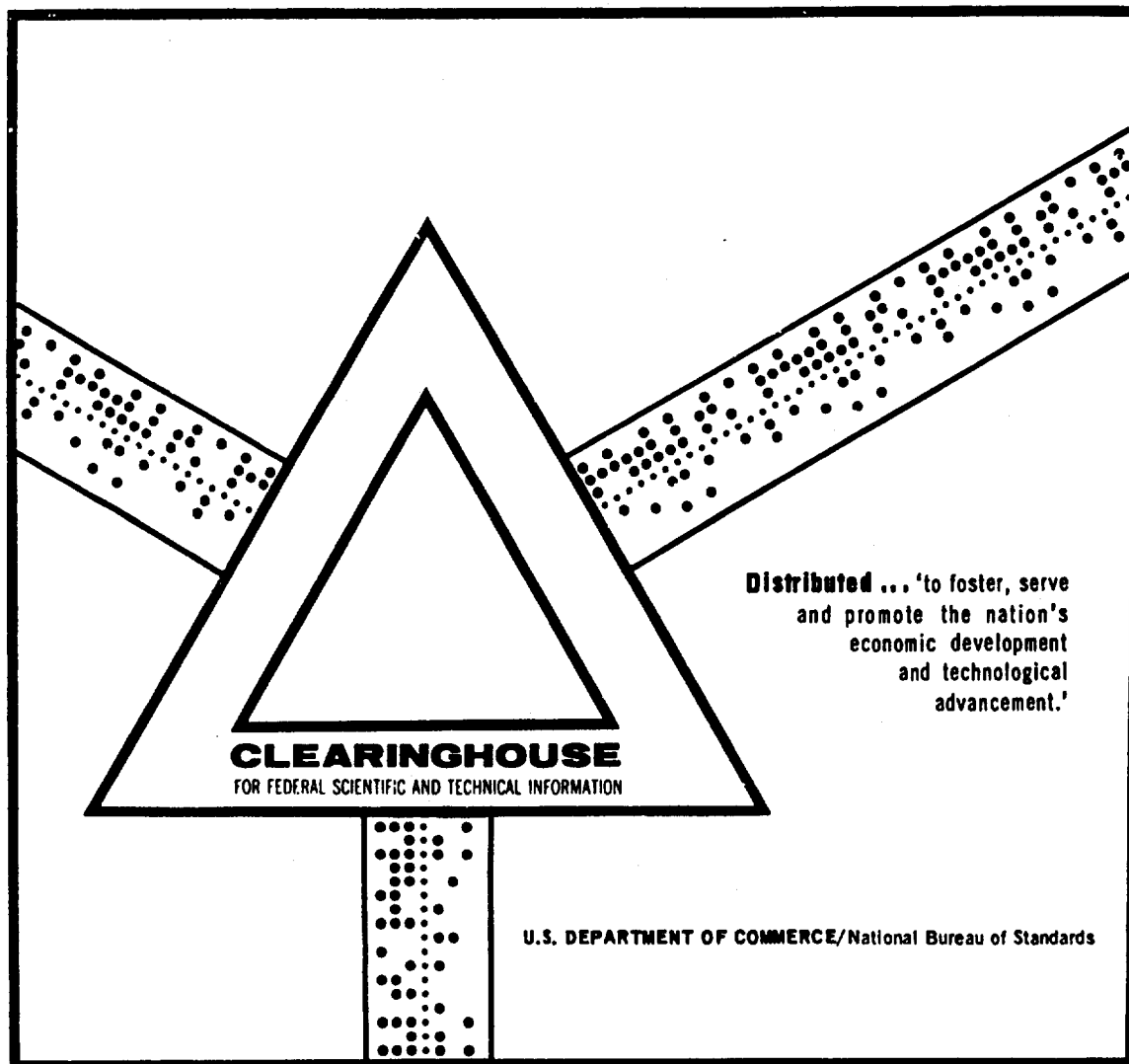AD 699 139

TWO EMPIRICAL CORRESPONDING STATES RELATION-
SHIPS FOR THE RATIO OF THE HEAT CAPACITIES OF
POLYMERS

R. W. Warfield, et al

Naval Ordnance Laboratory
White Oak, Maryland

21 October 1969

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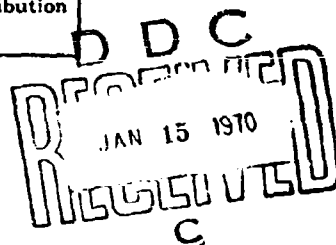R. W. Warfield
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TWO EMPIRICAL CORRESPONDING STATES RELATIONSHIPS FOR
THE RATIO OF THE HEAT CAPACITIES OF POLYMERS

Prepared by:
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M. C. Petree

ABSTRACT: Two empirical corresponding states . ationships between the ratio of the heat capacities C_p/C_v and the reduced tempe.ature parameters T/T_g and T/T_m have been found. These relationships are discussed in terms of the corresponding states behavior. These relationships are significant and useful in that the ratio C_p/C_v is a fundamental constant for a polymer and that a knowledge of the value of this ratio is indispensable for converting adiabatic data into the corresponding isothermal value.

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i

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TWO EMPIRICAL CORRESPONDING STATES RELATIONSHIPS FOR THE RATIO OF THE HEAT
CAPACITIES OF POLYMERS

The results presented in this report are significant in that calculated C_p/C_v
ratios are fundamental constants for polymers. Such data are indispensable
for converting dynamic mechanical data obtained under adiabatic conditions to
the corresponding isothermal values. The two corresponding states relationships
enable one to rapidly estimate values of C_p/C_v from glass transition temperature,
T_g, or crystalline melting point, T_m, data. The accuracy of the calculated
values of C_p/C_v is limited by the accuracy of the original measurements.

This investigation was accomplished under Independent Research Project IR-76,
Compressibility of Polymers.

                                        G. G. BALL
                                        Captain, USN
                                        Commander

                                        A. LIGHTBODY
                                        By direction

ii

CONTENTS

ILLUSTRATIONS

Figure   Title

1   Corresponding State Relationship Between C_p/C_v and T/T_g for Amorphous Polymers

2   Corresponding State Relationship Between C_p/C_v and T/T_M for Semicrystalline and Crystalline Polymers

TABLES

Table   Title

1   C_p/C_v of Polymers by Equation (1)

2   C_p/C_v of Polymers by Equation (3)

INTRODUCTION

Recently a number of workers have found that there are empirical corresponding state relationships between various polymer properties such as shear strength,[1] bulk modulus,[2a] thermal expansion,[2a,2b] viscosity,[3] and reduced temperature parameters. The status of these relationships is presently the subject of considerable discussion.[2b] It has been shown that in many cases such relationships may be employed to estimate the magnitude and to test the consistency and conformity of various quantities, particularly in cases where direct measurement is very difficult or impossible. Such relationships are also useful as a means of extrapolating values from limited experimental data.[3]

An exact definition of a corresponding state relationship is difficult,[2b] but a number of generalizations can be made. Van der Waals was the first to apply this principle to gases and liquids near the critical point[2b] in order to predict the properties of these substances from the more complete knowledge of other similar substances. As originally employed by Van der Waals, this principle is based on the reduction of variables by means of the critical constants. For example, he divided the P-V-T properties of different substances by the value at the critical point. With this mode of expression, material properties appear as dimensionless variables. Substances are then said to be in corresponding states when they are at the same reduced temperature ($T_R = T/T_C$), or pressure ($P_R = P/P_c$), or density $(\rho_R = \rho/\rho_c)$.

It is a modified version of this principle that we have used here. At present, no clearly defined critical points are known for polymers. We have employed the glass transition temperature, T_g, and the thermodynamic melting point, T_m, as alternate reference points. Thus, at pressures near zero one may say that polymers are in corresponding states when they are at the same reduced temperature ($T_R = T/T_g$) or ($T_R = T/T_m$).

Presented in this report are two new corresponding state relationships between the ratios of the heat capacity at constant pressure, C_p, and the heat capacity at constant volume, C_V, and the reduced temperature parameters T/T_g and T/T_m. Also presented are the calculated values of C_V and the ratio C_p/C_V for a large number of polymers.

RESULTS

Published and experimental thermodynamic data were collected and are presented in Tables 1 and 2. These data were used, as will be shown in the following section, to calculate C_V and C_p/C_V. Whenever possible, published data were chosen on polymers in the same physical and chemical state so that for any particular C_V calculation, all the input data are for systems of similar thermal and pressure history. Unfortunately, this is not easily accomplished and as a result some uncertainty is introduced into these calculations because of small differences in crystallinity, molecular weight, and thermal and pressure history.

Results of the C_V and C_p/C_V calculations are shown in Tables 1 and 2. Figure 1 shows the results obtained for amorphous systems by plotting the dimensionless parameters C_p/C_V vs. T/T_g. Figure 2 shows the results of plotting C_p/C_V vs.

T/T_m for crystalline and semicrystalline systems. In both figures the solid line is a least squares fit of the data points. In both cases the reduced temperature is defined as the ratio of the temperature at which the experimental measurements were made to the glass transition temperature, T_g, or crystalline melting point, T_m.

CALCULATION OF C_V

We have calculated C_V by means of two equations. Choice of the appropriate equation depends upon what experimental data are available. The first equation employed was derived several years ago[4].

$$c_V = c_p \left[\frac{1}{1 + \frac{T V_\ell^2 \alpha^2}{c_p J}} \right] \qquad (1)$$

where V_ℓ is the longitudinal (irrotational) sound velocity in centimeters per second, α is the cubic coefficient of expansion, C_p and C_V are the heat capacities at constant pressure and constant volume in cal/gm-degree, J is the mechanical equivalent of heat, 4.184×10^7 ergs/cal, and T is the absolute temperature.

To be absolutely correct, equation (1) should contain bulk wave velocity V_B instead of the irrotational velocity V_ℓ. In isotropic solids these two speeds are connected through Poisson's ratio, σ, by the relation

$$V_B^2 / V_\ell^2 = (1 + \sigma) / 3(1 - \sigma) \qquad (2)$$

For many polymers, experimental values of V_B are not available and values of σ are limited, and in those cases we have used the approximation given by equation (1). The error associated with this approximation will naturally vary somewhat with the type of polymer. The error, for example, would be quite small for rubbery polymers for which $\sigma \approx 1/2$ and $V_B^2 / V_\ell^2 = 1$. On the other hand, for a polymer such as polymethylmethacrylate for which $\sigma = 0.40$,[5] $V_B^2 / V_\ell^2 = 0.78$, the error in $C_p/C_V - 1$ is about -22%. In any event, one can expect the values obtained by equation (1) using V_ℓ will always be somewhat higher than the actual values. It should be noted that in three cases, that of polyisoprene, SBR rubber and butyl rubber, we have used data on the bulk wave velocity, V_B, and in these cases equation (1) is exact.

For those polymers for which sound velocity data are lacking and for which compressibility data are available, we have employed the standard thermodynamic relationship

$$c_V = c_p - \frac{V T \alpha^2 K}{\beta} \qquad (3)$$

2

where V is the specific volume in cm^3/gm, β is the compressibility in reciprocal atmospheres, α is the cubic coefficient of expansion, T is the absolute temperature, C_p and C_V are the heat capacities at constant pressure and constant volume, and K is a constant, 0.0242 cal/cm^3.

In addition to the calculated C_p/C_V values, two other values are given on Table 2. These values, for completely crystalline and completely amorphous polyethylene are theoretical values taken from a recent paper by Pastine.[63]

All the calculated values of C_V and C_p/C_V are given in Tables 1 and 2, together with the input data used in the calculations. The sources of the input data are indicated by superscripts beside the numerical values and refer to references.

It is of interest to note that in the case of polyisoprene experimental data are available to calculate C_V by both equations (1) and (3). In each case the calculated C_V is 0.384 cal/gm deg, which leads to a C_p/C_V ratio of 1.17.

DISCUSSION

The difference between C_p and C_V ranges from a percent or so for hard solids up to about 30% for liquids.[8] Inspection of the C_p/C_V ratios given in Tables 1 and 2 indicates that the values at 298°K range from 1.01 to 1.18. Thus, a prior assumptions as to the size of this ratio are, in the case of many polymers, not valid. It follows that failure to convert adiabatic values into the corresponding isothermal ones can, in many cases, result in significant errors.

Examination of the C_p/C_V values suggested that those amorphous systems which have high C_p/C_V ratios at 298°K are characterized by low glass transition temperatures, T_g. In addition, it was noted that for crystalline systems, those with high C_p/C_V ratios have low values for the crystalline melting point, T_m.

For each of these two classes of polymers we plotted C_p/C_V against the corresponding reduced temperature parameter T/T_g or T/T_m, and the results are shown in Figures 1 and 2.

It seems reasonable to attribute the scatter of the calculated data points in Figures 1 and 2 to two principal causes. Some of the scatter is a result of uncertainties in the input data. Unfortunately, the precision and accuracy of much of the input data is not known. However, we can generalize as follows: specific heat, volume, and temperature can almost always be determined to within 1½%. We have recently found that compressibility measurements made in this Laboratory are, in the case of amorphous polymers, precise to within 1%. These considerations would suggest that the C_V values calculated by equation (3) have a maximum error of about ±5%. Since longitudinal sound velocity measurements are usually accurate to within 2 to 3%, it would appear probable that those C_V calculations employing equation (1) also contain a maximum error of about ±5%.

The other and probably more significant source of scatter in Figures 1 and 2 lies in the implicit assumption that all the amorphous polymers considered are, to a greater or lesser degree, structurally similar at their glass transition temperature, T_g, or in the case of crystalline polymers, at their thermodynamic melting point, T_m. That this assumption has considerable validity is indicated by the plots of Figures 1 and 2. However, it must be pointed out that we have

considered polymers of many different types. For example, among the amorphous polymers are included linear and crosslinked systems, hard solids and soft rubbers. Some contain only carbon and hydrogen, while others contain, in addition, oxygen, nitrogen, chloride, and fluoride groups. In all cases we have plotted these polymers on the same coordinate system.

Ideally, we should plot data obtained for a series of polymers in which all the members are essentially the same. For example, a series of polystyrenes differing only in molecular weight or a series of acrylics differing the number of pendent groups on the main chain. Each of these series should, theoretically, yield an excellent corresponding states plot with a minimum of scatter. Regrettably, the necessary experimental data to construct plots on this basis does not exist. It would also be desirable to have data on the various polymers as a function of temperature.

In spite of the wide differences between many of the polymers, it appears that some relationship between corresponding states does exist and that the scatter in the points is in part a reflection of structural differences. This is particularly true in the case of the amorphous systems. When we consider the number of different polymers and the wide differences between them, if we had not obtained any scatter, one could question the validity of the data. In this connection, it should be noted that Greet and Magill[3] likewise encountered considerable scatter in their corresponding state plots relating viscosity and T/T_m. In short, the observed scatter in the plotted points does not appear unreasonable and does not significantly reduce the usefulness of the relationship.

We have fitted the plotted points in Figure 1, by the method of least squares, to an equation of the type

$$C_p/C_V = a + b_g \left(\frac{T}{T_g}\right) + c_g \left(\frac{T}{T_g}\right)^2 \tag{4}$$

where $a = 1.0000$, $b_g = -0.0449$, and $c_g = 0.1036$. As can be seen, equation (4) reproduces the experimental data to within an average deviation of 1.5%.

Likewise, the solid line in Figure 2 gives the result of fitting the data, by the method of least squares, to an equation of the type

$$C_p/C_V = a + b_m \left(\frac{T}{T_m}\right) + c_m \left(\frac{T}{T_m}\right)^2 \tag{5}$$

where $a = 1.0000$, $b_m = 0.0106$, and $c_m = 0.1216$.

It is of interest to note that Griskey[64] has recently employed the reduced temperature relationship, T/T_g, in a generalized equation of state for describing the pressure-volume-temperature behavior of polymers.

It seems worthwhile to mention here a possible explanation of corresponding states behavior in solids which has been given by Valvoda and Sprusil.[7] According to these workers, dimensionless quantities (such as C_p/C_V) will have the same value for different solids which have the same value of T/T_m, provided that:

4

1. At T = 0 the dimensionless ratios of physical quantities which depend on the potential can be calculated for all these solids from a single function.

2. The ratios of T_m to the cohesive energy density is the same for all the solids.

Whether or not this theory can be applied either strictly or loosely to polymers in general ought to be a subject of further investigation.

Perhaps the most useful application of the C_p/C_V ratios are in the conversion of adiabatic values to isothermal values. It is well established that volume changes which occur under the influence of longitudinal waves are adiabatic at most frequencies.[8] The critical frequency for the isothermal-adiabatic transition is somewhat dependent upon the dimensions of the specimen but, according to Ferry[9] can be as low as 0.1 cycle per second. Once the ratio C_p/C_V has been obtained for the polymer under consideration, data obtained under adiabatic conditions can be easily converted to the corresponding isothermal values. For example, in the case of bulk modulus data, B, the conversion is made by means of equation (6).

$$B_{is} = B_{ad} \frac{C_V}{C_p} \qquad (6)$$

where B_{is} and B_{ad} are the bulk moduli under isothermal and adiabatic conditions, respectively, and C_p and C_V are the heat capacities at constant pressure and constant volume.

For those polymers for which only T_g or T_m data are available, it should be possible to obtain a good estimate of the magnitude of the ratio C_p/C_V at 296°K by reference to the master curves on Figures 1 or 2.

CONCLUSIONS

Considerations of the data presented in this report have led to the following conclusions:

a. Two empirical corresponding state relationships between C_p/C_V and T/T_g and between C_p/C_V and T/T_m have been developed.

b. By means of these relationships a method is available to test the conformity and consistency of new data and to estimate the ratio C_p/C_V from a knowledge of only T_g or T_m.

c. The necessary data have been developed for converting adiabatic data to isothermal data.

RECOMMENDATIONS

It is recommended that additional input data on both amorphous and crystalline polymers be obtained so that the C_V calculations may be extended. With additional

data points, the validity of the two master curves so far obtained may be increased. It is also recommended that additional corresponding state relationships be developed in particular to test the conformity and consistency of experimental data on compressibility. If such a relationship could be developed, it might reduce the amount of experimental work necessary on new polymers.

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TABLE 1

c_p/c_v OF POLYMERS BY EQUATION (1)

Polymer	c_p, cal/gm deg	T, °K	Sound Velocity v, met/sec	Cubic Coefficient of Expansion α, deg^{-1}	c_v, cal/gm deg	c_p/c_v	T_G, °K	T_m, °K
Trans Polybutadiene	0.574[10]*	296	710[11]	7.8 x 10^{-4} [12]	0.553	1.04	259[19]	-
Polyethylene Terephthalate	0.262[13]	296	1700[14]	1.6 x 10^{-4} [15]	0.256	1.02	342[16]	543[22]
Isotactic Polypropylene	0.436[10]	296	1820[17]	4.8 x 10^{-4} [18]	0.390	1.12	-	438[19]
Polycaprolactam	0.375[20]	296	2330[21]	2.6 x 10^{-4} [21]	0.351	1.07	-	496[22]
Polyisoprene	0.450[23]	296	** 1560[24]	5.1 x 10^{-4} [24]	0.384	1.17	201[12]	-
SBR Rubber***	0.437[24]	296	** 1465[24]	6.6 x 10^{-4} [24]	0.376	1.16	221[24]	-
Butyl IIR ****	0.443[24]	296	** 1485[24]	5.7 x 10^{-4} [24]	0.397	1.12	210[24]	-

* Refers to reference number (source of data).
** Bulk Wave Velocity
*** Styrene-butadiene copolymer, 22.5% bound styrene
**** Isobutene-isoprene copolymer

TABLE 2

C_p/C_v OF POLYMERS BY EQUATION (3)

Polymer	C_p, cal/gm deg	Sp. Vol. v, cm³/gm	T, °K	Cubic Coefficient of Expansion α, deg⁻¹	Compressibility β, atm⁻¹	C_v, cal/gm	C_p/C_v	T_g, °K	T_m, °K
Polychlorotrifluoro-methylene	0.209(25)*	0.462(26)	298	1 x 10⁻⁴ (27)	5 x 10⁻⁵ (28)	0.208	1.01	-	493(19)
Polyoxymethylene	0.341(10)	0.70(29)	300	2.4 x 10⁻⁴ (30)	2.7 x 10⁻⁵ (28)	0.330	1.03	-	452(19)
Polycarbonate	0.282(10)	0.85(31)	298	1.5 x 10⁻⁴ (32)	4.1 x 10⁻⁵ (28)	0.279	1.01	423(19)	-
Polyvinyl Acetate	0.29(33)	0.855(31)	298	2.07 x 10⁻⁴(27)	1.4 x 10⁻⁵ (31)	0.272	1.07	302(12)	-
Polychloroprene	0.520(34)	0.882(34)	293	6 x 10⁻³(34)	4.8 x 10⁻⁵ (34)	0.440	1.10	228(34)	-
Polyepoxide + DMH	0.28(36)	0.847(29)	298	2.7 x 10⁻⁴(24)	3.8 x 10⁻⁵ (37)	0.268	1.05	340(36)	-
Polyhexamethylene Adipamide	0.310(38)	0.879(29)	298	2.4 x 10⁻⁴(34)	2.28 x 10⁻⁵(40)	0.294	1.05	-	539(41)
Poly-4-methyl-pentene-1	0.413(42)	1.20(42)	298	3.8 x 10⁻⁴(12)	4.8 x 10⁻⁵ (43)	0.387	1.07	302(12)	-
Polyvinylchloride	0.224(44)	0.75(31)	298	2.2 x 10⁻⁴(34)	3.0 x 10⁻⁵ (45)	0.216	1.04	355(12)	-
Atactic Polystyrene	0.301(4)	0.94(29)	298	2.35 x 10⁻⁴(4)	3.3 x 10⁻⁵ (28)	0.290	1.04	353(4)	-
Polymethyl Methacrylate	0.284(46)	0.855(47)	298	2.1 x 10⁻⁴(47)	1.5 x 10⁻⁵(48)	0.266	1.07	353(49)	-
Polybutene-1	0.479(50)	1.08(51)	298	4.5 x 10⁻⁴(52)	4.2 x 10⁻⁵(43)	0.440	1.09	248(19)	395(19)
Polyisobutylene	0.466(53)	1.1(54)	298	6.68 x 10⁻⁴(12)	4.10 x 10⁻⁵(54)	0.396	1.18	199(12)	-
Polyvinyl Alcohol	0.308(55)	0.767(56)	298	2.17 x 10⁻⁴(56)	1.5 x 10⁻⁵(56)	0.291	1.06	-	513(57)
Polytetrafluoroethylene	0.225(58)	0.45(59)	273	2.5 x 10⁻⁴(39)	2.87 x 10⁻⁵(39)	0.218	1.05	-	600(29)
Polyethylene Oxide	0.358(60)	0.825(61)	298	3.3 x 10⁻⁴(62)	2.14 x 10⁻⁵(43)	0.328	1.09	-	339(19)
Polyethylene							1.09(63)	243(19)	-
Polyethylene							1.07(65)	-	410(19)

* Refers to reference number (source of data).
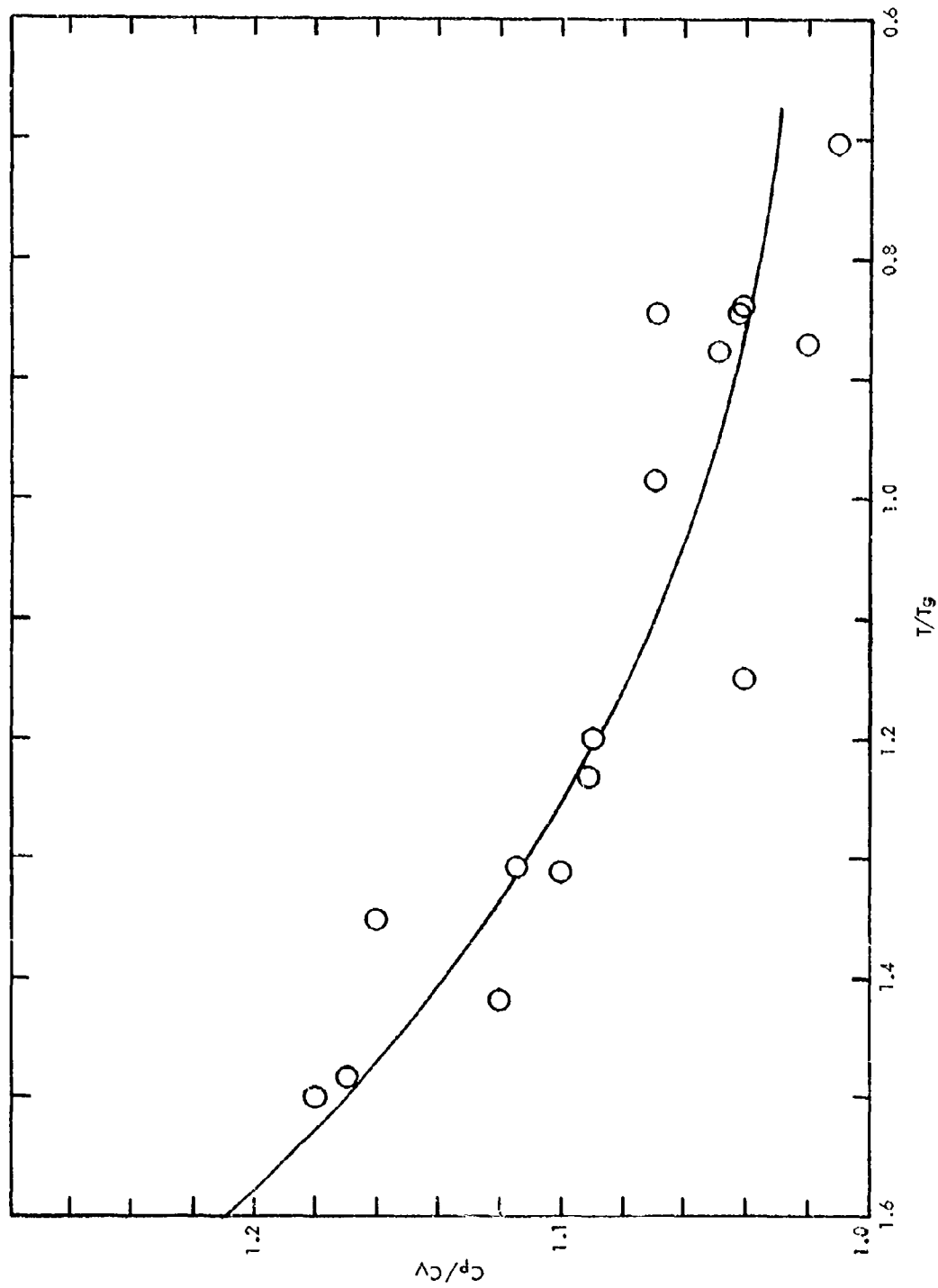** 15% of tris(dimethylaminomethyl)phenol tri(2-ethylhexote)

FIG. 1   CORRESPONDING STATE RELATIONSHIP BETWEEN C_P/C_V AND T/T_g FOR AMORPHOUS POLYMERS
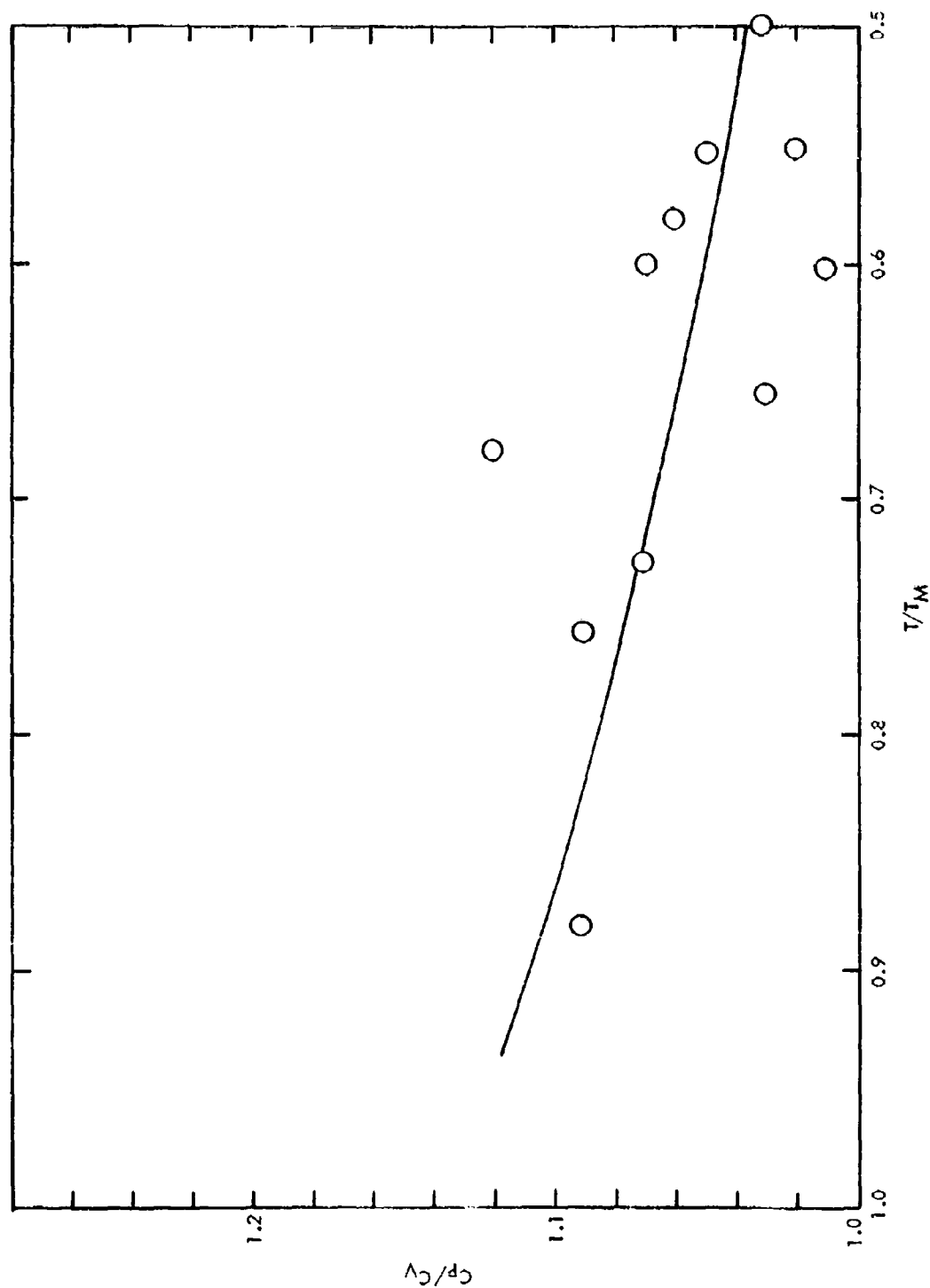
FIG. 2 CORRESPONDING STATE RELATIONSHIP BETWEEN C_P/C_V AND T/T_M FOR SEMICRYSTALLINE AND CRYSTALLINE POLYMERS

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13. ABSTRACT

Two empirical corresponding states relationships between the ratio of the heat capacities C_p/C_v and the reduced temperature parameters T/T_g and T/T_m have been found. These relationships are discussed in terms of the corresponding states behavior. These relationships are significant and useful in that the ratio C_p/C_v is a fundamental constant for a polymer and that a knowledge of the value of this ratio is indispensable for converting adiabatic data into the corresponding isothermal value.

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